

523, 540

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
19 February 2004 (19.02.2004)

PCT

(10) International Publication Number
WO 2004/014813 A2

(51) International Patent Classification⁷: **C03C 17/00**,
17/30, B32B 17/06, C09K 21/00, C01B 33/32

(74) Agents: **HALLIWELL, Anthony, Charles et al.**; Group
Intellectual Property Department, Pilkington plc, Pilkington
European Technical Centre, Hall Lane, Lathom, Ormskirk,
Lancashire L40 5UF (GB).

(21) International Application Number:
PCT/GB2003/003434

(22) International Filing Date: 6 August 2003 (06.08.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0218672.4 10 August 2002 (10.08.2002) GB

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(71) Applicant (*for all designated States except US*): **PILKINGTON PLC** [GB/GB]; Prescot Road, St. Helens, Merseyside WA10 3TT (GB).

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **HOLLAND, John, Richard** [GB/GB]; 36 Brick Kiln Lane, Rufford Ormskirk, Lancashire L40 1SZ (GB). **HOLDEN, David, William** [GB/GB]; 8 Milton Grove, Orrell, Wigan, Greater Manchester WN5 8HP (GB). **BOND, Stephen, Ian** [GB/GB]; 12 Shaftesbury Way, Burtonwood, Warrington, Cheshire WA5 4LB (GB). **VARMA, Karikath, Sukumar** [GB/GB]; 54 Palace Road, Birkdale, Southport, Merseyside PR8 2BE (GB).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: FIRE RESISTANT GLAZING

(57) Abstract: Fire resistant glazings comprise a fire resistant interlayer based upon a silicate waterglass are characterised by the incorporation of aluminium ions. The aluminate is incorporated as a solution which has been partially neutralised using a hydroxy-carboxylic acid which is preferably citric acid. The incorporation of aluminium provides glazings have improved fire resistance and impact properties

WO 2004/014813 A2

FIRE RESISTANT GLAZING

This invention relates to novel solutions useful in the production of fire resistant glazings comprising an alkali metal aluminate and a silicate waterglass, to methods for the preparation of those solutions and to the production of intumescent interlayers from those solutions which may be incorporated into fire resistant glazings.

Glass laminates incorporating an intumescent inorganic silicate interlayer sandwiched between two opposed panes of glass are sold under the trade marks PYROSTOP and PYRODUR by the Pilkington group of companies. When such laminates are exposed to a fire the inorganic interlayer intumesces and expands to form a foam. The foam provides a thermally insulating layer which protects the pane of glass remote from the fire so that the structural integrity of the glass unit which acts as a barrier preventing the propagation of the fire is maintained for a longer period. Glass laminates incorporating such intumescent interlayers have been used successfully as fire resistant glass structures. These laminates may comprise more than two panes of glass sandwiching more than one intumescent interlayer. Laminates comprising up to eight intumescent interlayers have been employed. These multi layered laminates are relatively thick and correspondingly expensive.

The intumescent inorganic layer is normally formed from a sodium silicate waterglass or a mixture thereof with a potassium silicate waterglass. The layer is commonly formed by preparing a solution of the waterglass (or waterglasses), spreading that solution on the surface of the glass and drying excess water from the solution so as to form the intumescent inorganic layer.

USP 4190698 discloses fire resistant glazings comprising an intumescent inorganic layer obtained by drying a waterglass solution. The authors suggest the addition of various additives to the waterglass solution including urea, polyhydric alcohols, monosaccharides, polysaccharides, sodium phosphate, sodium aluminate, borax, boric acid and colloidal silica. There is no specific disclosure of the addition of an aluminate to a waterglass solution.

We have discovered that the addition of sodium aluminate to a waterglass solution as proposed in USP 4190698 does not produce a solution which is useful in the production of fire resistant glazings. The solutions are unstable and form a precipitate

immediately or on standing. Since the dried interlayer is used as part of a glazing it must be optically clear. The presence of particulate material such as this precipitate is not acceptable.

Applicants have discovered that it is possible to produce a clear stable solution comprising an aluminate and a silicate waterglass which can be used in the production of fire resistant glazings by partially neutralising the aluminate with a hydroxy carboxylic acid prior to mixing it with the waterglass. Thus from one aspect this invention provides a clear stable solution useful in the production of fire resistant glazings comprising an alkali metal silicate waterglass and a water soluble aluminate which has been partially neutralised with a hydroxy carboxylic acid.

The water soluble aluminate is preferably an alkali metal aluminate such as lithium aluminate, potassium aluminate, caesium aluminate and most preferably sodium aluminate. Other water soluble aluminates notably ammonium aluminate and alkyl ammonium aluminates may also be employed.

The carboxylic acid is preferably a hydroxy carboxylic acid and more preferably an α -hydroxy carboxylic acid. Examples of preferred carboxylic acids include tartaric acid, malic acid, gluconic acid, lactic acid, saccharic acid and most preferably citric acid.

The waterglasses useful in the compositions of this invention are preferably sodium silicate waterglasses. The preferred sodium silicate waterglasses are those wherein the weight ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ is at least 1.6:1 e.g 2.0:1, more preferably at least 2.5:1 and most preferably at least 2.85:1. Sodium silicate waterglass solutions wherein the weight ratio of $\text{SiO}_2 : \text{Na}_2\text{O}$ varies between 2.0:1 and 4.0:1 are available as articles of commerce. Specifically solutions wherein this ratio is 2.0:1, 2.5:1 and 2.85:1 3.0:1 and 3.3:1 are available as articles of commerce. Waterglasses having any particular weight ratio of $\text{SiO}_2 : \text{Na}_2\text{O}$ may be produced by blending these commercially available waterglass solutions. Sodium silicate waterglasses having a weight ratio of $\text{SiO}_2 : \text{Na}_2\text{O}$ of 2.0:1, 2.5:1 and 2.85:1 may incorporate a higher proportion of aluminate and produce a glass which combines good fire resistance properties with good impact resistant properties. Sodium silicate waterglasses having a higher weight ratio of SiO_2 to Na_2O e.g 3.0 :1 ; 3.3:1 or 3.9:1 are able to incorporate a smaller proportion of aluminate and produce fire resistant glasses with relatively superior fire resistant properties and relatively inferior

impact resistant properties. In a preferred embodiment the fire resistant glazings of the present invention are produced from a sodium silicate waterglass having a weight ratio of $\text{SiO}_2 : \text{Na}_2\text{O}$ of from 2.5:1 to 3.0:1.

Potassium silicate and lithium silicate waterglasses may also be used in the compositions of this invention. In a preferred embodiment these waterglasses will be used as a partial replacement for the sodium silicate waterglasses. In general the molar ratio of sodium to potassium and/or lithium in the waterglass solution will be at least 2:1.

In particular preferred embodiment the waterglass solution used in the present invention comprise a mixture of sodium silicate waterglass and a potassium silicate waterglass. The molar ratio of sodium ions to potassium ions in these mixtures is preferably at least 4:1. Where a potassium silicate waterglass is employed it is preferably one where the weight ratio $\text{SiO}_2 : \text{K}_2\text{O}$ is in the range 1.43:1 to 2.05:1.

The solutions of this invention may further comprise one or more polyhydric compounds which are known to be useful in existing intumescent interlayers. Polyhydric compounds which have been proposed for this use include glycerol, glycerine or a derivative of glycerine or a sugar. The most commonly used polyhydric compound and the preferred polyhydric compound for present use is glycerol.

In order to be useful in the production of intumescent interlayers the solution of this invention should preferably be clear, stable and capable of being dried to form a useful intumescent interlayer. The stability of the solution is affected by the composition of the solution and the methods used in its preparation. The utility of any particular solution may be determined by experiment. The stability of the solutions decreases as the amount of aluminate present increases. However the fire resistance of the interlayer increases in proportion to the amount of aluminate present. The amount of aluminate which is incorporated into the solution will preferably represent a compromise between these two properties. The molar ratio of silicon to aluminium may vary from as much as 100:1 to 20:1 but preferably is in the range 20:1 to 35:1 and more preferably in the range 25:1 to 32:1.

A second significant factor which affects the utility of the solutions of this invention is the weight ratio of silica to alkali metal oxide. Increasing the proportion of

silica reduces the stability of the solution and is undesirable. The higher ratios of silicon to alkali metal are preferred since this increases the flow point of the dried interlayer which is an important factor influencing the performance of a glazing incorporating such an interlayer in fire testing. Generally we prefer that the weight ratio of silica to alkali metal oxide is in the range 2:1 to 4:1; more preferably 2.5:1 to 4:1

The solutions of the present invention must be clear. They are prepared by mixing the various components in a manner which produces a clear stable solution which may then be dried to form a clear stable intumescent layer.

We prefer that the solutions are prepared using a process which comprises as a first step partially neutralising the aluminate with the hydroxy carboxylic acid. This neutralisation may be carried out by adding a hydroxycarboxylic acid solution to an aqueous solution of the aluminate. As the presence of excessive quantities of water may destabilise the silicate solutions of the invention and because in any event excess water is an additional load on the drying process used to form the intumescent interlayer the aluminate solution will preferably contain as high a solids content as is compatible with the production of a clear stable solution. The partially neutralised aluminate solution may typically comprise from 20 to 45% by weight of solids.

The hydroxy carboxylic acid solution may be added to the aluminate as a solid but more usually it will be added as a solution. The solution may be an aqueous solution. In the preferred embodiments where the solutions of this invention comprise a polyhydroxy compound which is preferably glycerol the hydroxy carboxylic acid may be dissolved in the polyhydroxy compound and the resulting solution used to partially neutralise the aluminate.

The addition of the acid solution to the aluminate solution is preferably continued until the solution has a pH in the range 9.0 to 11.0 and more preferably in the range 9.5 to 10.0. The neutralisation should be carried out with thorough mixing and in a manner such that the temperature of the reaction mixture is not allowed to rise excessively and is preferably maintained below 50°C.

Solutions which comprise a water soluble aluminate, a hydroxy carboxylic acid and a polyhydric compound which is preferably glycerol are believed to be novel and comprise a further aspect of the invention.

The partially neutralised aluminate solution may be added to a solution comprising an alkali metal silicate waterglass to form a solution according to the present invention. The mixing of the aluminate with the waterglass must be carried out in a controlled manner so as to avoid the formation of any precipitate. We prefer to add the aluminate to the waterglass at a controlled rate with thorough mixing. The resulting clear stable solutions comprising a water soluble aluminate, a hydroxy carboxylic acid, a polyhydric compound and an alkali metal silicate waterglass are believed to be novel and comprise a further aspect of the invention. In particular solutions which have been produced by mixing an aluminate which has been partially neutralised with an hydroxycarboxylic acid with a waterglass solution are believed to be novel

The resulting solutions may be used in the production of fire resistant glazings using known techniques. In one existing process the solutions may be spread upon the surface of a glass sheet which is provided with an edge barrier which retains the solution on the surface of the glass. The quantity of solution employed will vary with the desired thickness of the dried interlayer. The quantity needed to produce an interlayer of any particular thickness may be determined by routine experiment.

The solution is then dried under carefully controlled conditions of temperature and humidity so as to ensure the production of a clear transparent interlayer which is free from bubbles and other optical imperfections. The dried interlayers generally comprise from 10 to 35% by weight of water. The aluminium content of the dried interlayer is generally in the range 0.1% to 5.0% by weight preferably from 0.1% to 1.0% by weight. We have discovered that the presence of the aluminium improves the performance of glazings into which the interlayer is incorporated in terms of their fire resistance and their mechanical impact resistance properties.

The thickness of the dried interlayer will generally be in the range 0.1 to 2.0 mm preferably from 0.5 to 2.0 mm. The formations of thicker interlayers requires a longer drying time and is thereby disadvantageous. Thinner interlayers can be produced using shorter drying times. A glass laminate having a thicker interlayer may be produced by bringing two sheets of glass each having a relatively thin interlayer having say a thickness of from 0.5 mm to 1.0 mm into face to face contact so as to form a laminate having an intumescent interlayer which is from 1.0mm to 2.0 mm thick.

Flat glass sheets of various thickness may be used in the laminates of the present invention. Typically sheets of soda lime float glass having a thickness of from 2.0 mm to 4.0 mm are employed. An edge barrier formed from a suitable material such as a clay may be provided at the edges of the glass so as to retain the waterglass solution on the surface of the glass.

The edge barrier is normally cut away at the completion of the drying process to leave a glass sheet having a dried interlayer on one surface. A laminate may be formed by placing a second glass sheet on top of the interlayer. In another embodiment the second glass sheet may itself be one having an intumescent interlayer on one surface thereof. Mounting this second sheet on top of the first sheet so that the two fire resistant interlayers are in contact with each other produces a laminate having a relatively thick interlayer. Mounting the second sheet so that the interlayer is on its upper surface and subsequently providing a third glass sheet on top of that second interlayer produces a laminate having two interlayers mounted between three panes of glass. Laminates having as many as eight interlayers may be produced.

In an alternative process the solutions of this invention may be poured onto the surface of the substrate and dried to form an intumescent fire resistant interlayer which is sufficiently strong to be removed from the substrate in the form of a transparent film. The film may then be placed between two sheets of glass to form a fire resistant glass laminate. A variety of substrates may be employed in processes of this type examples being glass sheets, metal sheets and polymeric materials such as PTFE and polyolefins such as polypropylene. Where the substrate is clear and transparent, e.g when the substrate is a clear polymeric film, having a dried interlayer on one surface thereof the substrate may be incorporated into a glass laminate and thereby produce a fire resistant laminate without the need to separate the dried interlayer from the substrate.

The invention is illustrated by the following example

Example 1

A solution comprising a sodium aluminate, a sodium silicate waterglass, a potassium silicate waterglass and citric acid was made up using the following components:-

- 1 A solution of a sodium silicate waterglass having a weight ration $\text{SiO}_2:\text{Na}_2\text{O}$ of 2.85:1 and comprising 40% by weight of solids, sold by INEOS as Crystal 96.
- 2 A solution of a potassium silicate waterglass having a weight ration of $\text{SiO}_2:\text{K}_2\text{O}$ of 1.43:1 comprising 52.4% by weight of solids; sold by INEOS as Crystal K120 potassium silicate
- 3 An aqueous solution of sodium aluminate comprising 38.0% by weight solids sold by Nordisk Aluminate
- 4 Glycerol - an 87% by weight solution in water
- 5 Citric acid - reagent grade

A partially neutralised aluminate solution wase made up as follows :-

First 5 parts by weight of citric acid were added to 10 parts by weight of glycerol with stirring so that the citric acid dissolved. The resulting solution is added slowly with vigorous stirring to 8.86 parts by weight of the sodium aluminate solution. The temperature of the solution was maintained below 50°C throughout the addition. The resulting solution had a pH of 9.5.

A waterglass solution comprising a sodium silicate , a potassium silicate and glycerol was made up by mixing 151.7 parts by weight of Crystal 96 with 44.3 parts by weight of Crystal K120 and 10.5 parts by weight of glycerol.

The partially neutralised aluminate solution was then added to the waterglass solution. The addition was carried out by slowly adding the aluminate solution with thorough mixing using a Silverson high shear mixer. The resulting solution was clear and was stable on storage at room temperature.

This solution was then applied to the surface of a sheet of float glass having an edge barrier around its perimeter in a quantity of 4 kilograms of solution per square metre of glass. The glass sheet was placed in an oven and dried over a prolonged period in a controlled atmosphere until the water content of the solution had reduced to 26% by

weight. A clear interlayer having a depth of approximately 1.3mm had formed on the surface of the glass.

The edge barrier was cut away and a second sheet of float glass having a thickness of 3mm was placed on top of the interlayer to produce a glass laminate. Pieces of this laminate were tested for Fire Resistance according to B.S. 476 Part 20/2 and mechanical impact performance according to B.S 6206 Class C. Two pieces were subject to the fire test and both passed with times of 33 minutes and 30 minutes. Four pieces were tested for impact performance and all were rated at least a safe pass.

Example 2

A partially neutralised aluminate solution was prepared in the same manner as in Example 1. The aluminate solution was added to a solution of a sodium silicate waterglass having a weight ratio $\text{SiO}_2:\text{Na}_2\text{O}$ of 3.3:1 and comprising 37% by weight solids. The quantity added was such as to provide 2 parts by weight of sodium aluminate to 100 parts of sodium silicate. The atomic ratio of silicon to aluminium in the solution was approximately 56:1.

The solutions were mixed in the same manner as recited in example 1. The resulting solution was clear and was stable on storage over a period of weeks.

The solution was poured onto a sheet of float glass, dried, laminated and tested for Fire Resistance in the same manner as is recited in Example 1. The fire resistance time was 66 minutes.

Example 3

Example 2 was repeated with the exception that a higher proportion of aluminate was used to provide 3 parts of sodium aluminate to 100 parts of sodium silicate. The atomic ratio of silicon to aluminium was 38:1. The resulting solution was clear and stable over a period of weeks.

Example 4

Example 1 was repeated using a sodium silicate waterglass having a weight ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ of 3.9:1 in form of an aqueous solution comprising 28% by weight of solid material. The amount of partially neutralised aluminate solution added was sufficient to provide an atomic ratio of silicon to aluminium of 96:1. The solution was clear and stable over an extended period. It could be dried on glass to form a clear interlayer. It was noted that if the proportion of aluminate was increased so that the atomic ratio of silicon to aluminium was 64:1 the resulting solution was unstable and was not tested further.

Example 5

Example 1 was repeated using a sodium silicate waterglass having a weight ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ of 2.5:1 in the form of an aqueous solution comprising 41% by weight of solid material. The amount of aluminate added was sufficient to provide an atomic ratio of silicon to aluminium of 33:1. The solution was clear and remained clear after storage at 70°C for two weeks.

The solution was poured onto a sheet of 3m float glass and dried to form a clear interlayer which was approximately 1.4mm thick. This glass was laminated with a second sheet of float glass and the laminate tested for fire and impact resistance using the procedures described in example 1. The fire resistance time was 39 minutes. The laminate safely passed the impact test described in B.S 6206 class C.

CLAIMS

- 1 A clear stable aqueous solution comprising an alkali metal silicate waterglass, a water soluble aluminate and a hydroxy carboxylic acid.
- 2 A solution according to claim 1 characterised in that the water soluble aluminate is an alkali metal aluminate.
- 3 A solution according to either of claims 1 or 2 characterised in that the water soluble aluminate is a sodium aluminate.
- 4 A solution according to any of claims 1 to 3 characterised in that the hydroxycarboxylic acid is an α -hydroxy carboxylic acid.
- 5 A solution according to claim 4 characterised in that the hydroxycarboxylic acid is selected from the group comprising tartaric acid, malic acid, gluconic acid, lactic acid, saccharic acid and citric acid.
- 6 A solution according to claim 5 characterised in that the hydroxycarboxylic acid is citric acid.
- 7 A solution according to any of the preceding claims characterised in that the alkali metal silicate waterglass having a weight ratio $\text{SiO}_2:\text{M}_2\text{O}$ of from 2.0:1 to 4.0:1 where M represents an alkali metal cation.
- 8 A solution according to claim 7 characterised in that the sodium silicate waterglass has a weight ratio $\text{SiO}_2:\text{Na}_2\text{O}$ of from 2.5:1 to 3.0:1.
- 9 A solution according to either of claims 7 or 8 characterised in that it further comprises a potassium silicate waterglass
- 10 A solution according to claim 9 characterised on that the potassium silicate has a weight ratio $\text{SiO}_2:\text{K}_2\text{O}$ of from 1.43:1 to 2.05:1.

- 11 A solution according to either of claims 9 or 10 characterised in that the molar ratio of sodium ions to potassium ions is at least 2:1.
- 12 A solution according to any of the preceding claims characterised in that the molar ratio of silicon to aluminium is in the range 20:1 to 35:1.
- 13 A solution according to claim 12 characterised in that the molar ratio of silicon to aluminium is in the range 25:1 to 32:1.
- 14 A solution according to any of the preceding claims characterised in that the weight ratio of silica to alkali metal oxide is in the range 2:1 to 4:1.
- 15 A solution according to any of the preceding claims characterised in that it further comprises a polyhydric compound.
- 16 A solution according to claim 15 characterised in that the polyhydric compound is glycerol.
- 17 A clear intumescent interlayer characterised in that it has been produced by drying a solution according to any of claims 1 to 16 under controlled conditions.
- 18 An interlayer according to claim 17 characterised in that it comprises from 10 to 35% by weight of water.
- 19 An interlayer according to either of claims 17 or 18 characterised in that it comprises from 0.1 to 5.0% by weight of aluminium.
- 20 An interlayer according to any of claims 17 to 19 characterised in that the interlayer has a thickness of from 0.5 to 2.0 mm.

- 21 A glass sheet having an interlayer according to any of claims 17 to 20 on one surface thereof.
- 22 A laminated glazing which comprises one or more interlayers according to any of claims 17 to 20 and two or more sheets of glass.
- 23 A clear stable solution comprising a water soluble aluminate, a hydroxycarboxylic acid and a polyhydroxy compound.
- 24 A solution according to claim 23 characterised in that the aluminate is sodium aluminate.
- 25 A solution according to either of claims 23 or 24 characterised in that the hydroxycarboxylic acid is citric acid.
- 26 A solution according to any of claims 23 to 25 characterised in that the polyhydroxy compounds is glycerol.
- 27 A solution according to any of claims 23 to 26 characterised in that it has a pH in the range 9.0 to 11.0.